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- (71) **Applicant:** THE JOHNS HOPKINS UNIVERSITY [US/US]; 3400 N. Charles Street, Baltimore, Maryland 21218 (US).
- (72) **Inventors:** WEIHS, Timothy P.; 6905 Marlborough Road, Baltimore, Maryland 21212 (US). OVERDEEP, Kyle; 6009 Prescott Avenue, Baltimore, Maryland 21212 (US). LAKSHMAN, Shashank Vummidi; 2619 Maryland Avenue, Apt. 1, Baltimore, Maryland 21218 (US). WAIN-WRIGHT, Elliot; 3017 Barclay Street, Baltimore, Maryland 21218 (US).
- (74) **Agent:** RYAN, Louisa; Johns Hopkins Technology Ventures, 1812 Ashland Avenue, Suite 110, Baltimore, Maryland 21205 (US).

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(54) **Title:** COMPOSITE REACTIVE MATERIALS WITH INDEPENDENTLY CONTROLLABLE IGNITION AND COMBUSTION PROPERTIES

(57) **Abstract:** The present invention is directed to composite particles that react with a small and adjustable input energy. The ignition threshold depends primarily upon reactant spacing and chemistry, not overall particle size. Combustion properties, such as burn duration and temperature, are controlled by adjusting particle size or reactant composition. The best performance is achieved by selecting reactants with strong intermetallic formation reaction and that combust in different phases (condensed vs gaseous). These particles are fabricated by various methods, including physical vapor deposition, or ball milling. The concept of purposefully decoupling ignition and combustion properties by fabricating particles where ignition is determined by reactant spacing and/or composition and combustion is determined by adjusting particle size and/or composition is described. Combinations of specific reactants, such as Al, Zr, Ti, Mo, Mg, B, Li, etc. exhibit dual-phase combustion, and/or enhance combustion through prevention of terminating species. Ternary additions are used to form gaseous species.



**COMPOSITE REACTIVE MATERIALS WITH INDEPENDENTLY
CONTROLLABLE IGNITION AND COMBUSTION PROPERTIES**

GOVERNMENT RIGHTS

5 **[0001]** This invention was made with government support under HDTRAA1-11-1-0063
and HDTRA1-15-1-0006 awarded by the Defense Threat Reduction Agency. The government
has certain rights in the invention.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This application claims the benefit of U.S. Provisional Patent Application No.
10 62/252,870 filed November 9, 2015, which is incorporated by reference herein, in its entirety.

FIELD OF THE INVENTION

[0003] The present invention relates generally to composite particles. More particularly,
the present invention relates to composite reactive materials with independently controllable
ignition and combustion properties.

15 **BACKGROUND OF THE INVENTION**

[0004] Traditional energetic materials like HMX, RDX, and TNT etc. are commonly used
in propellants, pyrotechnics, and explosives due to their high reaction rates and high degree
of reaction completion. However, these traditional energetic materials have low energy
densities when compared to metal based fuels. Metal fuels such as Al, B, Ti, Mg, Zr etc. have
20 higher enthalpies of combustion and hence higher energy densities. Thus, metal-based fuels
are often added to propellants, pyrotechnics, and explosives to deliver more thrust or energy.
The use of such metal-based additives, though, is limited due to slow reaction rates, poor
reaction completion, and other material-specific drawbacks.

[0005] Most metal-based fuel particles have a protective oxide coating which forms naturally as the fresh metal surface is exposed to air. As a result of this protective layer, micron-sized metal particles have long ignition delays and need to be heated to high temperatures to react. The ignition of metal particles is usually controlled by the

5 heterogeneous oxidation reaction leading to self-sustained combustion, which is relatively slow compared to the reaction of HMX, RDX etc. To ease ignition, metal-based fuels have been fabricated in nanoscale diameters and have found some viable applications. However, nano powders can be pyrophoric. Nano powders can also agglomerate and tend to have poor flow characteristics; thus storing and handling becomes challenging.

10 **[0006]** Looking at specific chemistries, aluminum combustion is characterized by the formation of oxide caps on the surface of the burning metal particle. The presence of the oxide caps tends to cause an asymmetric flame and shift the vapor phase combustion to a surface reaction limited process. This leads to the premature termination of combustion, leaving the metal fuels only partially reacted. Boron combustion in humid environments
15 forms undesirable “HOB” by-products that have lower heats of formation than the fully oxidized particles. As a result, they tend to provide low energy densities and energy yields. Other fuels like Mg, Zr, Ti, etc. are pyrophoric even on the micron-scale, and hence have few commercial applications as fuel particles.

[0007] Layered or composite particles have been fabricated via physical vapor deposition
20 (PVD), ball milling and by rolling and grinding etc. to reduce or control ignition thresholds through an exothermic reaction. However, these materials have seen limited application or commercial development and the associated literature does not teach independent control of, and independent optimization of, both ignition and combustion properties. One example

employs the use of Group 4 or 5 elements in conjunction with other materials to form intermetallic compounds. The heat of formation from this reaction is strong enough to vaporize other components to initiate combustion. The patent describes the use of blends consisting of individual reactant particles. Therefore, the ignition threshold is likely to be high and difficult to tune in this case due to a large reactant spacing that is controlled by the particle size.

[0008] Alloying elements such as Mg, Li etc. that have low vaporization temperatures have been used to enhance ignition. However, they simultaneously increase the rate of combustion and thereby reduce burn time. Thus, they do not offer independent control of ignition and combustion. Thermite compositions have been used as an alternative to pure metals for many energetic applications. Thermite compositions consist of both fuel and oxidizers in close proximity, and as a result they show advanced ignition and combustion properties. However, due to the close proximity of the fuel and oxidizer, these compositions tend to age i.e. partially react over time thus reducing their energy density. Additionally, thermite compositions require careful storage and handling solutions which limit their commercial use. They also offer lower energy densities than similar pure fuel or metallic particles that would draw oxygen from the environment, rather than carrying the oxygen within the fuel itself. Alternative techniques where metal particles are coated with organic compounds that act as a passivating layer have received some interest. While these coatings provide a passivating layer, they ultimately reduce the energy density of the material.

[0009] Recent developments in the synthesis of engineered reactive particles that overcome the apparent limitations of traditional metal fuels have resulted in increasing use of these fuels for various propellant, pyrotechnics and explosives applications. Some of the

applications, such as bio-agent defeat, require fuels that are easy to ignite and have long burn times that result in high thermal kill. However, the above technologies that help reduce the ignition threshold to ease ignition result in either lower burn durations or a lack of control of burn duration. Thus, there is a need to engineer particles where the mechanisms that control ignition and combustion durations and temperatures can be controlled independently to create truly tailored reactive fuel particles.

BRIEF DESCRIPTION OF THE FIGURES

[0010] FIG. 1 illustrates a graphical view of ignition temperature as a function of bilayer thickness for Al:Zr foils of varying thicknesses.

10 [0011] FIG. 2 illustrates an image view of nylon mesh substrates used to make PVD particles.

[0012] FIGS. 3A and 3B illustrate a view of back scattered electron images of the cross-sections of Al:Zr particles prepared by ball milling. The lighter components correspond to Zr and the darker components correspond to Al. FIG. 3A illustrates an image view of particles that were milled for 1 hour with a ball to powder ratio (BPR) of 5. FIG. 3B illustrates an image view of particles that were milled for 1 hour with a BPR of 10.

[0013] FIG. 4 illustrates a graphical view of DSC and DTA results of Al-8Mg:Zr composites fabricated by various fabrication methods and conditions.

[0014] FIG. 5 illustrates a graphical view of DTA results for composite particles prepared by ball milling various ratios of Al to Zr with a BPR 5 and a milling duration of 1hr.

[0015] FIG. 6 illustrates an image view of Al:Zr₃ particles ignited on a heated filament, displaying the characteristic microexplosions associated with the combustion of zirconium.

[0016] FIG. 7 illustrates a backscattered electron image of a rapidly quenched 3Al:2Zr composite particle on a silicon wafer.

5 [0017] FIG. 8 illustrates a backscattered electron image of a rapidly quenched 2Al:3Zr composite particle/agglomerate on a silicon wafer. The bright metallic particles are partially covered by a darker, porous oxide. The lighter halo on the silicon substrate likely indicates Al gas-phase combustion resulting in the deposition of Al₂O₃.

[0018] FIG. 9A illustrates a graphical view of bomb calorimetry results showing the heat
10 released from burning Al:Zr and Al-8Mg:Zr foils in 1 atm of air. By varying the foil thickness, which is equivalent to particle size, heat production remains high for Mg-containing foils, but drops off for Al:Zr foils without the vaporizing species.

[0019] FIG. 9B illustrates a graphical view of foil burn duration, measured using high
15 speed videography, as a function of foil thickness. As thickness increases, burn duration increases.

[0020] FIG. 10 illustrates a graphical view of temperature measurements of burning particles ignited on a heated filament as a function of combustion time.

SUMMARY

[0021] The foregoing needs are met, to a great extent, by the present invention, wherein in
20 one aspect a composite particle includes two or more elemental or metallic alloy reactants whose spacing and average composition are controlled. This is done to enable and tune an

exothermic formation reaction that leads to extensive combustion of the product where the combustion reaction is controlled through the use of chemistry and/or particle size.

[0022] In accordance with an aspect of the present invention, the average reactant spacing is between 100 nm and 10 μ m, so as to tune (e.g. lower) the threshold for igniting the formation

5 reaction. The chemistry for the formation reaction includes the primary reactant taking the form of Al or an Al alloy and the secondary reactant taking the form of one chosen from a group of B, Co, Ti, Zr, Hf, Nb, or V and the average composition ranges from 10Al:X to Al:10X wherein

X is the secondary reactant. The chemistry for the formation reaction includes the primary reactant taking the form of B or a B alloy and the secondary reactant taking the form of one

10 chosen from a group of Hf, Mg, Mo, Nb, Ta, Ti, V, or Zr and the average composition ranges from 10B:X to B:10X wherein X is the secondary reactant. The chemistry for the formation reaction includes the primary reactant taking the form of C or a C alloy and the secondary

reactant taking the form of one chosen from a group of Hf, Nb, Si, Ta, Ti, V, or Zr and the average composition ranges from 10C:X to C:10X wherein X is the secondary reactant. The

15 chemistry for the formation reaction includes the primary reactant taking the form of Si or a Si alloy and the secondary reactant taking the form of Mo, Nb, V, Zr, Ti, Hf, or Ta and the average composition ranges from 10Si:X to Si:10X wherein X is the secondary reactant. The composite

particle contains at least one component that undergoes vapor phase combustion such as Al, B, Mg, Ca, Li, K, or Na for enhanced combustion. The composite particle has a ternary addition

20 that is one chosen from a group of Mg, Ca, Li, K, or Na for enhanced *ignition*, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of

primary reactants. The composite particle has a ternary addition that could be one of, but is not limited to Mg, Ca, Li, K, or Na for enhanced *combustion*, wherein the atomic percentage of the

alloying element is varied between 0 and 25% within the system of primary reactants. The

composite particle has a binary chemistry and one or more ternary additions that are chosen from a group of Mg, Ca, Li, K, or Na for modified reaction pathways that minimize the formation of unwanted low energy byproducts during combustion. The composite particle's average diameter is between 100 nm and 500 μ m so as to tune the combustion duration independently from ignition thresholds.

[0023] In accordance with another aspect of the present invention, a composite particle includes two or more elemental or metallic alloy reactants whose spacing is controlled so as to tune and enable an exothermic formation reaction and whose chemistry is chosen so as to lead to a combustion reaction that is dual phase (condensed and vapor).

[0024] In accordance with yet another aspect of the present invention, the average reactant spacing of the composite particle is between 100 nm and 10 μ m, so as to tune the threshold for igniting the formation reaction independently from combustion behavior. The average particle diameter is between 100 nm and 500 μ m, so as to tune the combustion duration independently from ignition thresholds. The chemistry for the formation reaction comprises the primary vapor phase reactant taking the form of Al or an Al alloy and the secondary solid phase reactant taking the form of one chosen from a group consisting of Ti, Zr, Ta, Nb, V, or Hf and the average composition ranges from 10Al:X to Al:10X where X is the secondary reactant. The chemistry for the formation reaction comprises the primary vapor phase reactant taking the form of B or a B alloy and the secondary solid phase reactant taking the form of one chosen from a group consisting of Ti, Zr, Ta, Nb, V, or Hf and the average composition ranges from 10B:X to B:10X where X is the secondary reactant. The composite particle contains one component that enhances *vapor phase* combustion and is one chosen from a group consisting of Al, B, Mg, Ca, Li, K, or Na. The composite particle has a ternary addition that is one chosen from a group of Mg, Ca, Li, K, or Na for modified reaction pathways that minimize the

formation of unwanted low energy byproducts during combustion. The composite particle has a ternary addition that is one chosen from a group consisting of Mg, Ca, Li, K, or Na for enhanced *ignition*, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants. The composite particle has a ternary addition
5 that is one chosen from a group of Mg, Ca, Li, K, or Na for enhanced *vapor phase* combustion, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants. The composite particle has a ternary addition that could be one of, but is not limited to Mg, Ca, Li, K, or Na for enhanced *condensed phase* combustion, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system
10 of primary reactants.

[0025] In accordance with another aspect of the present invention, a composite particle comprising two or more reactants, where one of the elements is alloyed with a more volatile element to enhance combustion, and the atomic percentage of the alloying element is varied to control combustion properties.

15 **[0026]** In accordance with yet another aspect of the present invention, one reactant is chosen from a group of Al, B, C, and Si and the enhancing alloy is one chosen from a group of Li, K, Na, Mg, or Ca. The chemistry is chosen so as to lead to a combustion reaction that is dual phase (condensed and vapor).

[0027] In accordance with still another aspect of the present invention, a composite particle
20 includes two elemental or metallic alloy reactants whose spacing, composition, and particle size are controlled such that the particles are non-pyrophoric even at particle sizes <30um, non-toxic, experience low agglomeration compared to nanoaluminum, and/or have a shelf life of over a year. The composite particle is formed from one element chosen from the group of Al, B, or Si, plus a second element from the group Ti, Zr, or Hf, and has an average diameter

<100um. The composite particle is formed from reactants that have a spacing between 100 nm and 10 μm , so as to tune the threshold for igniting the formation reaction.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0028] The presently disclosed subject matter now will be described more fully hereinafter

5 with reference to the accompanying Drawings, in which some, but not all embodiments of the inventions are shown. Like numbers refer to like elements throughout. The presently disclosed subject matter may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. Indeed, many
10 modifications and other embodiments of the presently disclosed subject matter set forth herein will come to mind to one skilled in the art to which the presently disclosed subject matter pertains having the benefit of the teachings presented in the foregoing descriptions and the associated drawings. Therefore, it is to be understood that the presently disclosed subject matter is not to be limited to the specific embodiments disclosed and that modifications and
15 other embodiments are intended to be included within the scope of the appended claims.

[0029] The present invention is directed to composite particles that are able to react with a

small input energy. The ignition threshold depends primarily upon the reactant spacing and chemistry, not the overall particle size. Combustion properties, such as burn duration and temperature, can then be controlled by adjusting particle size or reactant composition. The
20 best performance is achieved by selecting reactants with a strong intermetallic formation reaction, and ones that combust in different phases (condensed vs gaseous). These particles can be fabricated by various methods, including physical vapor deposition, or ball milling. The proposed concept purposefully focuses on decoupling ignition and combustion properties by fabricating particles where ignition is determined by reactant spacing and/or composition,

while combustion is determined by adjusting particle size and/or composition. Combinations of specific reactants, such as Al, Zr, Ti, Mo, Mg, B, Li, etc. exhibit dual-phase combustion, and/or enhance combustion through the prevention of terminating species. Ternary additions can be used to form gaseous species.

5 **[0030]** More particularly, the present invention is directed to the use of composite particles that have either layers of alternating reactive elements or inclusions of one reactive element in a matrix of the other reactive element. Multilayered particles produced by physical vapor deposition (PVD) have alternating layers of two or more components with large exothermic heats of mixing. When these particles are initiated with an external stimulus, the individual
10 layers react to form an intermetallic compound and uniformly heat the particles to very high temperatures where full-fledged combustion is enabled and sustained. The energy density needed to ignite a self-sustained formation reaction within the particles and rate at which the particles heat up are controlled by the reactant spacing i.e. the thickness of the individual layers, as well as the overall chemistry of the particles. Unlike typical metal particles, the
15 ignition temperature is *not* a function of total size, as demonstrated in FIG. 1, where the ignition temperature of nanocomposite foils are provided as a function of bilayer spacing for foils of two different total thicknesses. Foils are roughly 50 mm long, 10 mm wide, and 10-60 μm thick, and therefore exhibit some different combustion behavior from particles, but the relationship between ignition temperature and reactant spacing is the same. Comparing the
20 points for 40 μm thick Al:Zr foils (red) and 20 μm thick Al:Zr foils (black), the total thickness does not influence the ignition temperature, and ignition is therefore decoupled from foil/particle size. Although a great deal of work has been performed on the Al:Zr system, other binary combinations of reactants are possible as well, as listed in Table 1.

[0031] FIG. 1 illustrates a graphical view of ignition temperature as a function of bilayer thickness for Al:Zr foils of varying thicknesses. Ignition temperature is defined as the lowest temperature at which 100% of the foil fragments ignite, and is measured by dropping fragments onto a hot plate of known temperature.

5 **Table 1.**

Chemistries	Adiabatic Reaction Temperature (K) (w/phase changes)	Gravimetric Heat of Combustion (kJ/g)	Volumetric Heat of Combustion (kJ/cm ³)
Al + 2B	1253	43.4	113.1
Al + Co	1913	12.5	64.8
2Al + Ti	1643	25.7	85.6
2Al + Zr	1923	19.1	76.9
2B + Hf	3653	11.9	98.1
2B + Mg	1706	41.5	84.3
2B + Mo	1533	17.2	104.5
2B + Nb	2793	19.4	114.0
2B + Ta	2766	11.3	117.3
2B + Ti	3498	31.9	114.9
2B + V	2960	28.2	118.1
2B + Zr	3673	21.0	95.9
C + Hf	4223	7.9	69.1
C + Nb	3003	12.8	79.0
C + Si	1914	32.5	74.8
C + Ta	2678	7.3	83.0
C + Ti	3523	22.3	79.6
C + V	2121	18.6	78.7
C + Zr	3800	14.4	67.1
2Si + Mo	1854	16.9	78.8
3Si + 5Nb	2518	13.6	85.0
2Si + V	2023	24.2	83.1
Si + 2Zr	2198	14.8	71.6

[0032] Table 1 shows potential binary combinations of reactants with high theoretical merit based on having adiabatic reaction temperatures > 1200 K for their formation reaction and relatively large gravimetric and/or volumetric heats of combustion for their reactions

with oxygen. The heats of combustion for each combination were calculated based on 100% oxidation of each component.

[0033] PVD particles can be fabricated by magnetron sputtering onto a mesh, as shown in FIG. 2. FIG. 2 illustrates an image view of nylon mesh substrates used to make PVD

5 particles. (Left) A micrograph of a square nylon mesh substrate with a fiber diameter of 50 μm . (Middle) This substrate geometry results in vapor deposited multilayer particles with a

length three times their diameter. (Right) The microstructure of the particles consists of alternating layers of reactive components, such as Ni and Al or Zr and Al. In this case, alternating layers of Al and Zr are deposited on a nylon mesh. By varying the rate of

10 deposition and the rotation of the substrates, the Al and Zr layer thicknesses are controlled.

The overall dimensions of the particles are controlled by choosing weaves of specific dimensions and by the total duration of the deposition. Composite particles of the same nominal chemistry can also be fabricated by ball milling Al and Zr powders together. Unlike PVD particles, this method produces a distribution of Zr inclusions within an Al matrix and

15 this distribution controls the ignition characteristics of the fabricated particles. The size and distribution of Zr inclusions depends on the milling duration and the grinding media,

including the ball to powder weight ratio (BPR) and the size of the milling balls. FIGS. 3A and 3B are examples of reactive composite particles fabricated via ball milling. These images show particles that were prepared by ball milling a blend of Al and Zr powders with a BPR of

20 5 (A), and with a BPR of 10 (B). FIGS. 3A and 3B clearly show that the size of Zr inclusions is much larger (and hence the average spacing of Zr and Al reactants is much larger) for samples prepared with a BPR of 5 when compared to those prepared with a BPR of 10. The

control shown here for Al and Zr can be applied to many other systems, such as those listed in Table 1.

[0034] FIGS. 3A and 3B illustrate a view of back scattered electron images of the cross-sections of Al:Zr particles prepared by ball milling. The lighter components correspond to Zr and the darker components correspond to Al. FIG. 3A illustrates an image view of particles that were milled for 1 hour with a ball to powder ratio (BPR) of 5. FIG. 3B illustrates an image view of particles that were milled for 1 hour with a BPR of 10.

[0035] Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA) were used to gauge the reaction sensitivity of fabricated materials. The experiments were performed under Ar gas with a constant heating rate of 40 K/min. FIG. 4 illustrates the results from the thermal analysis of Al-8Mg:Zr composites fabricated by PVD as well as by ball milling. It is important to note that while the overall chemistry of the composites are the same, the reactivity is distinctly different. As expected, both the PVD foils and the PVD particles have a sharp heat release due to the highly uniform nanoscale layering of their reactive components. The PVD particles have slightly broader peaks compared to the PVD foils, due to their inherent crescent shape in which the edges of the particles have a smaller layer thickness compared to their centers. Ball-milled particles, however, have very broad and shorter exothermic peaks due to the wide distribution of the reactant inclusion size. By changing the parameters for ball milling (ball size, ball to powder ratio, milling time, etc.) one can vary the dominant reactant size and the average reactant spacing, and thereby produce particles with tunable reactivity and ignition thresholds. The reactivity or rate of component mixing is also dependent on the average sample chemistry. For example, as the relative amounts of Al and Zr are varied within the Al:Zr system, different intermetallic

products form, the rate of mixing or reactivity will vary, and ignition sensitivity will differ.

FIG. 5 depicts DTA results for ball-milled Al-Zr particles with varying Al to Zr ratios but fabricated under similar conditions. The size and onset of the first major exothermic peak changes based on the average composition of the samples. These variations indicate changes in reactivity and ignition thresholds for the particles (Note: the DTA results have been shifted vertically for comparison purposes.) Hence, by changing the average chemical composition or the average reactant spacing within the particle, one can tune the reactivity or ignition sensitivity of the composite particles. FIG. 4 illustrates a graphical view of DSC and DTA results of Al-8Mg:Zr composites fabricated by various fabrication methods and conditions.

FIG. 5 illustrates a graphical view of DTA results for composite particles prepared by ball milling various ratios of Al to Zr with a BPR 5 and a milling duration of 1 hr. (Note: the values of the DTA results have been shifted vertically for comparison purposes.)

[0036] Combustion of reactive particles was studied in a qualitative way by coating a 36 gauge nichrome filament with reactive particles and resistively heating the filament with an

external power supply. The coated particles ignite upon heating and combust in an aerosolized cloud around the filament. This combustion phenomenon was recorded using a NAC Memrecam HX-6 high-speed camera. FIG. 6 illustrates the combustion of composite Al:3Zr particles. The initial intermetallic reaction between Al and Zr heats the particles to high temperatures where combustion of Al and Zr is observed. During Zr combustion, nitrogen dissolves into the molten metal solution rapidly, followed by a much slower oxygen dissolution. As the oxygen concentration increases, a stoichiometric metal oxide and α Zr precipitate out of the metal-oxygen-nitrogen solution, resulting in the rapid release of nitrogen. The sudden release of nitrogen is accompanied by jumps in brightness and micro-

explosions, as seen in FIG. 6. This unique combustion property of Group 4 elements such as Ti, Zr and Hf, enables the use of large particles that will break apart into smaller pieces during combustion and burn more efficiently. These group 4 metals can also be used as one of the alloying species in composite particles, due to their high oxygen and nitrogen solubility, to enhance combustion characteristics of the composites. FIG. 6 illustrates an image view of Al:Zr₃ particles ignited on a heated filament, displaying the characteristic microexplosions associated with the combustion of zirconium.

[0037] FIG. 7 illustrates a backscattered electron image of a rapidly quenched 3Al:2Zr composite particle on a silicon wafer. FIG. 8 illustrates a backscattered electron image of a rapidly quenched 2Al:3Zr composite particle/agglomerate on a silicon wafer. The bright metallic particles are partially covered by a darker, porous oxide. The lighter halo on the silicon substrate likely indicates Al gas-phase combustion resulting in the deposition of Al₂O₃. The EDS data collected for the particle displayed in FIG. 7 indicates that the particle contained 43.01 at % O, 16.63 at.% Al and 36.32 at.% of Zr. The initial particle had an Al to Zr ratio of 60:40, and the rapidly quenched particle contained a ratio of 31.5:68.95. This indicates that Al vaporized from the particle and underwent combustion in the vapor phase while Zr underwent solid-state combustion. Aluminum combustion is characterized by the formation of AlO in the vapor state followed by the subsequent precipitation of stoichiometric Al₂O₃ on the surface of the particle, which can be seen as the dark covering on the particle in FIG. 8. Both Al and Zr have unique modes of combustion, and by varying the ratio of Al to Zr the combustion duration can be controlled. Since vapor phase combustion of Al is observed, the flux of material reacting in the vapor phase can be changed by varying the

amount of Al. As a result, the combustion duration, flame speed and also the combustion temperature can be varied.

[0038] By including other alloying elements such as Li, Na, Mg, Ca etc., that combust in the vapor phase, the combustion properties of the composite particles are further tuned. For example, by using an alloy of Al and Mg as one of the reactants, the Mg will vaporize during the combustion process due to its high vapor pressure and low solubility with the forming oxides. The volatility of the alloying species creates vacancies and porosity in the combusting particle and enhances combustion in the vapor state. The former effect increases oxygen transport in the particle and this improves combustion efficiency, as shown in Table 2. This table also shows that the theoretical gravimetric heat of combustion does not differ by a significant amount as Al is replaced with Mg, but the measured heats of combustion does increase by 25%. This shows that the theoretical loss in energy density is outweighed by the benefit of improved oxidation.

Table 2.

Composition	Heat of Combustion in 1 atm O ₂ (kJ/g)	Theoretical Maximum Heat of Combustion (kJ/g)
Al:Zr	6.18 ± 0.043	16.73
Al-8Mg:Zr	7.73 ± 0.283	16.52
Al-38Mg:Zr	7.62 ± 0.160	15.69

[0039] The effect of replacing Al with alloys of Al and varying amounts of Mg are shown in Table 2. The heats of combustion were measured for foils (50 mm x 10 mm x 40 μm) as a

proof of concept by reacting in a bomb calorimeter containing 1 atm of oxygen. The values show that the addition of small amount of a volatile component (Mg) improves heat output. Theoretical values were calculated based on 100% oxidation of each component. Note that combustion of foils is less efficient than the combustion of particles.

5 **[0040]** The improvements in oxygen diffusion that are gained by including a vaporizing species like Mg have further important consequences. By improving the penetration of oxygen into the burning particle, combustion efficiency is less dependent upon particle size, as demonstrated in FIG. 9A, where the heat output from Al:Zr foils are compared to the heat output from Al-8Mg:Zr foils reacting in air. Al:Zr foils (darker squares) combust less
10 efficiently as they become larger, but with the addition of Mg (lighter circles), the heat output is largely unaffected by foil size. This is important because it allows for the fabrication of larger particles to increase burn duration (FIG. 9B) without sacrificing heat output. It is important to note that the data shown was collected using nano-layered foils rather than particles, simply because they are easier to fabricate and observe, and the trends found for
15 foils are expected to hold true for analogous particles. FIG. 9A illustrates a graphical view of bomb calorimetry results showing the heat released from burning Al:Zr and Al-8Mg:Zr foils in 1 atm of air. By varying the foil thickness, which is equivalent to particle size, heat production remains high for Mg-containing foils, but drops off for Al:Zr foils without the vaporizing species. FIG. 9B illustrates a graphical view of foil burn duration, measured using
20 high-speed videography, as a function of foil thickness. As thickness increases, burn duration increases.

[0041] Furthermore, it is also possible for the presence of volatile species to increase the combustion temperature of the system. Control of the combustion temperature could be

achieved by varying the concentration and species of the composite particle. Temperatures of the burning ball milled particles in air was measured using an Aventes UV-VIS spectrometer. The particle temperature was determined by fitting the grey body emission with Plank's equation. FIG. 10 depicts the temperature measurements of burning particles ignited on the heated filament. The grey curve represents the combustion temperature of particles with a high ratio of Al and Mg that burn predominantly in the vapor phase. The black curve represents the combustion temperature of particles that are Zr rich and void of Mg. Since Zr burns in the solid phase, the resulting combustion temperature is much lower when compared to the grey curve. As a result, the feasibility to tune the combustion temperature by varying the chemistry is demonstrated. FIG. 10 illustrates a graphical view of temperature measurements of burning particles ignited on a heated filament as a function of combustion time. The grey curve represents the combustion temperature of 4(Al₂₀Mg):Zr particles whereas the black curve represents the combustion temperature of Al:3Zr particles.

[0042] While these volatile additives are dangerous at small particle sizes and on their own, they are passivated due to the comparatively stable nature of the primary reactants, for example, Al or C. The vaporizing species may also cause significant surface porosity upon combustion, increasing the surface area available for oxidation and thereby removing the need to manufacture as-is nanoscale particles with high surface area. This enhances the stability of the material in storage and the handling of the material by avoiding pyrophoric behavior.

[0043] Some of the alloying elements such as Li, Na, K, Mg and Ca may help prevent the formation of terminating species. For example, when boron burns in an environment containing water vapor and carbon dioxide (common products of combustion from primary

fuels such as HMX and RDX), the combustion is characterized by the formation of HOBO species. These HOBO species prevent the formation of the highly exothermic boron oxide and thereby result in a premature termination of combustion. The use of alloying elements such as Li, Na and K, that can react with water vapor and carbon dioxide to form stable
5 oxides, carbonates, or hydroxides, could prevent the formation of HOBO species.

[0044] Although the present invention has been described in connection with preferred embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention as defined in the appended claims.

CLAIMS

1. A composite particle comprising two or more elemental or metallic alloy reactants whose spacing and average composition are controlled so as to enable and tune an exothermic formation reaction that leads to extensive combustion of the product where the combustion reaction is controlled through the use of chemistry and/or particle size.

2. The composite particles of claim 1 wherein the average reactant spacing is between 100 nm and 10 μ m, so as to tune (e.g. lower) the threshold for igniting the formation reaction.

3. The composite particle of claim 1 wherein the chemistry for the formation reaction comprises the primary reactant taking the form of one chosen from a group consisting of Al or an Al alloy and the secondary reactant taking the form of one chosen from a group consisting of B, Co, Ti, Zr, Hf, Nb, or V and the average composition ranges from 10Al:X to Al:10X wherein X is the secondary reactant.

4. The composite particle of claim 1 wherein the chemistry for the formation reaction comprises the primary reactant taking the form of one chosen from a group consisting of B or a B alloy and the secondary reactant taking the form of one chosen from a group consisting of Hf, Mg, Mo, Nb, Ta, Ti, V, or Zr and the average composition ranges from 10B:X to B:10X wherein X is the secondary reactant.

5. The composite particle of claim 1 wherein the chemistry for the formation reaction comprises the primary reactant taking the form of one chosen from a group of a C or a C alloy and the secondary reactant taking the form of one chosen from a group

consisting of Hf, Nb, Si, Ta, Ti, V, or Zr and the average composition ranges from 10C:X to C:10X wherein X is the secondary reactant.

6. The composite particle of claim 1 wherein the chemistry for the formation reaction comprises the primary reactant taking the form of one chosen from a group consisting of Si or a Si alloy and the secondary reactant taking the form of one chosen from a group consisting of Mo, Nb, V, Zr, Ti, Hf, or Ta and the average composition ranges from 10Si:X to Si:10X wherein X is the secondary reactant.

7. The composite particles of claim 1 wherein the composite particle contains at least one component that undergoes vapor phase combustion such as one chosen from a group consisting of Al, B, Mg, Ca, Li, K, or Na for enhanced combustion.

8. The composite particle of claim 1 wherein the composite particle has a ternary addition that is one chosen from a group consisting of Mg, Ca, Li, K, or Na for enhanced *ignition*, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants.

9. The composite particle of claim 1 wherein the composite particle has a ternary addition that could be one of, but is not limited to one chosen from a group consisting of Mg, Ca, Li, K, or Na for enhanced *combustion*, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants.

10. The composite particle of claim 1 wherein the composite particle has a binary chemistry and one or more ternary additions that are chosen from a group consisting of Mg, Ca, Li, K, or Na for modified reaction pathways that minimize the formation of unwanted low energy byproducts during combustion.

11. The composite particle of claim 1 further comprising composite particles whose average diameter is between 100 nm and 500 μm so as to tune the combustion duration independently from ignition thresholds.

12. A composite particle comprising two or more elemental or metallic alloy reactants whose spacing is controlled so as to tune and enable an exothermic formation reaction and whose chemistry is chosen so as to lead to a combustion reaction that is dual phase (condensed and vapor).

13. The composite particle of claim 12 further comprising a composite particle in which the average reactant spacing is between 100 nm and 10 μm , so as to tune the threshold for igniting the formation reaction independently from combustion behavior.

14. The composite particle of claim 12 further comprising a composite particle in which the average particle diameter is between 100 nm and 500 μm , so as to tune the combustion duration independently from ignition thresholds.

15. The composite particles of claim 12 wherein the chemistry for the formation reaction comprises the primary vapor phase reactant taking the form of Al or an Al alloy and the secondary solid phase reactant taking the form of one chosen from a group consisting of Ti, Zr, Ta, Nb, V, or Hf and the average composition ranges from 10Al:X to Al:10X where X is the secondary reactant.

16. The composite particle of claim 12 wherein the chemistry for the formation reaction comprises the primary vapor phase reactant taking the form of B or a B alloy and the secondary solid phase reactant taking the form of one chosen from a group consisting of Ti, Zr, Ta, Nb, V, or Hf and the average composition ranges from 10B:X to B:10X where X is the secondary reactant.

17. The composite particle of claim 12 wherein the composite particle contains one component that enhances *vapor phase* combustion and is one chosen from a group consisting of Al, B, Mg, Ca, Li, K, or Na.

18. The composite particle of claim 12 having a ternary addition that is one chosen from a group consisting of Mg, Ca, Li, K, or Na for modified reaction pathways that minimize the formation of unwanted low energy byproducts during combustion.

19. The composite particle of claim 12 wherein the composite particle has a ternary addition that is one chosen from a group consisting of Mg, Ca, Li, K, or Na for enhanced *ignition*, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants.

20. The composite particle of claim 12 having a ternary addition that is one chosen from a group consisting of Mg, Ca, Li, K, or Na for enhanced *vapor phase* combustion, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants.

21. The composite particles of claim 12 having a ternary addition that could be one of, but is not limited to Mg, Ca, Li, K, or Na for enhanced *condensed phase* combustion, wherein the atomic percentage of the alloying element is varied between 0 and 25% within the system of primary reactants.

22. A composite particle comprising two or more reactants, where one of the elements is alloyed with a more volatile element to enhance combustion, and the atomic percentage of the alloying element is varied to control combustion properties.

23. The composite particle of claim 22 wherein one reactant is chosen from a group consisting of Al, B, C, and Si and the enhancing alloy is one chosen from a group consisting of Li, K, Na, Mg, or Ca.

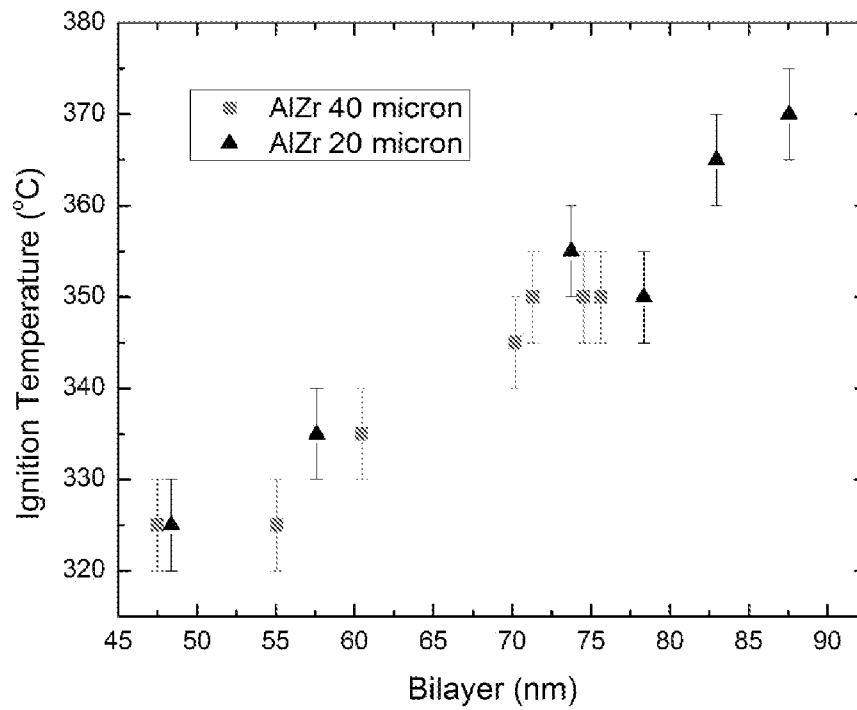
24. A composite particle of claim 22 whereas the chemistry is chosen so as to lead to a combustion reaction that is dual phase (condensed and vapor).

25. A composite particle comprising two elemental or metallic alloy reactants whose spacing, composition, and particle size are controlled such that the particles are non-pyrophoric even at particle sizes <30um, non-toxic, experience low agglomeration compared to nanoaluminum, and/or have a shelf life of over a year.

26. The composite particle of claim 25 further comprising a composite particle formed from one element chosen from the group of Al, B, or Si, plus a second element from the group Ti, Zr, or Hf, and has an average diameter <100um.

27. The composite particle of claim 25 further formed from reactants that have a spacing between 100 nm and 10 μm , so as to tune the threshold for igniting the formation reaction.

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**FIG. 1**

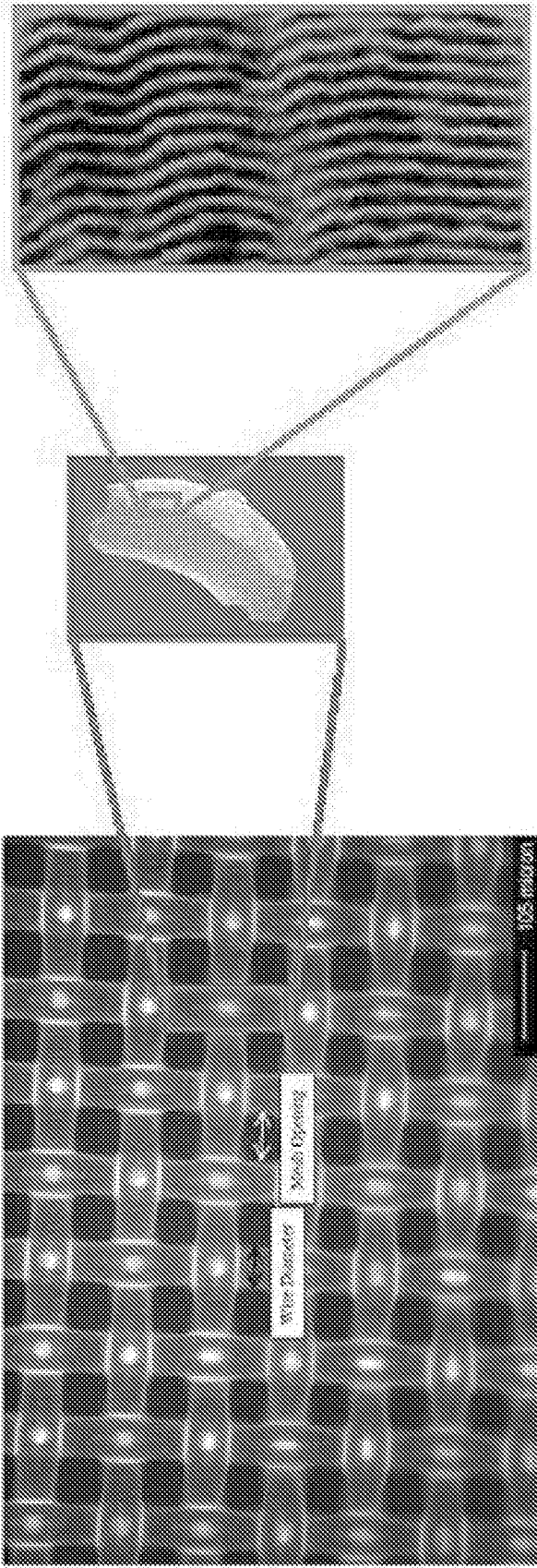


FIG. 2

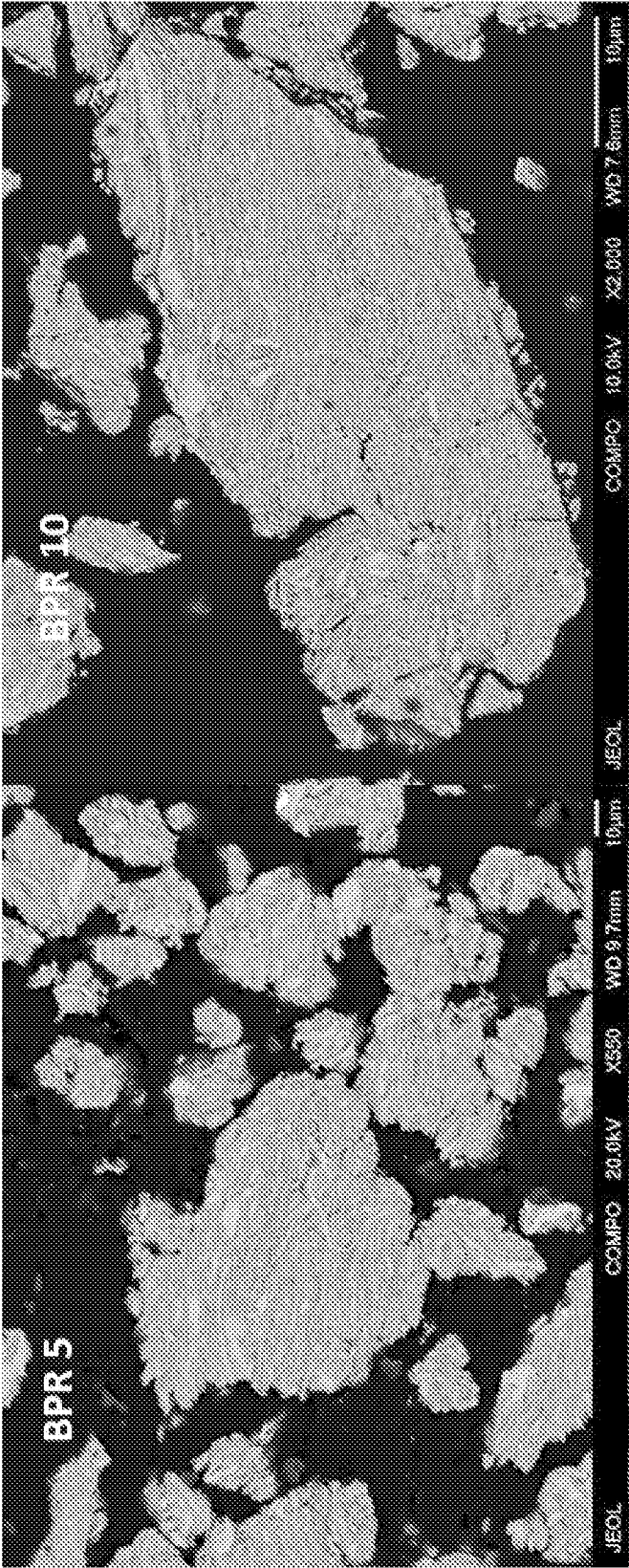
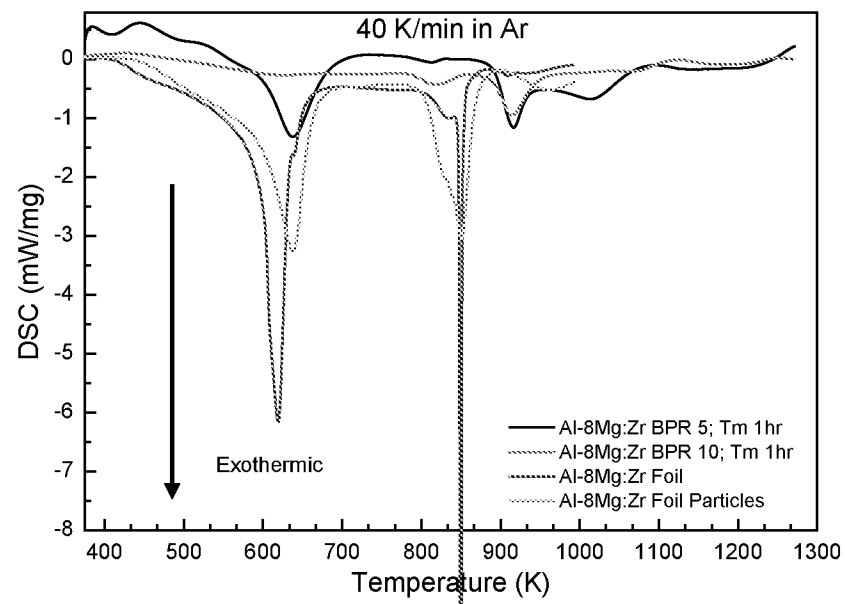
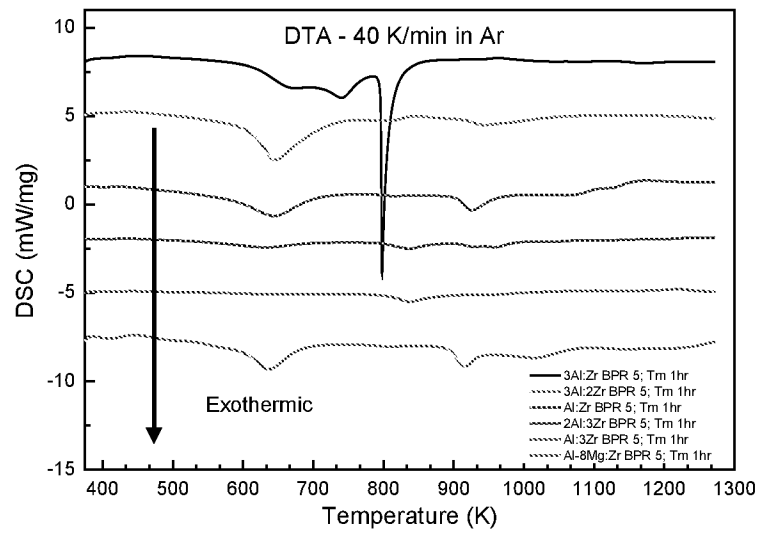


FIG. 3A

FIG. 3B

**FIG. 4**

**FIG. 5**

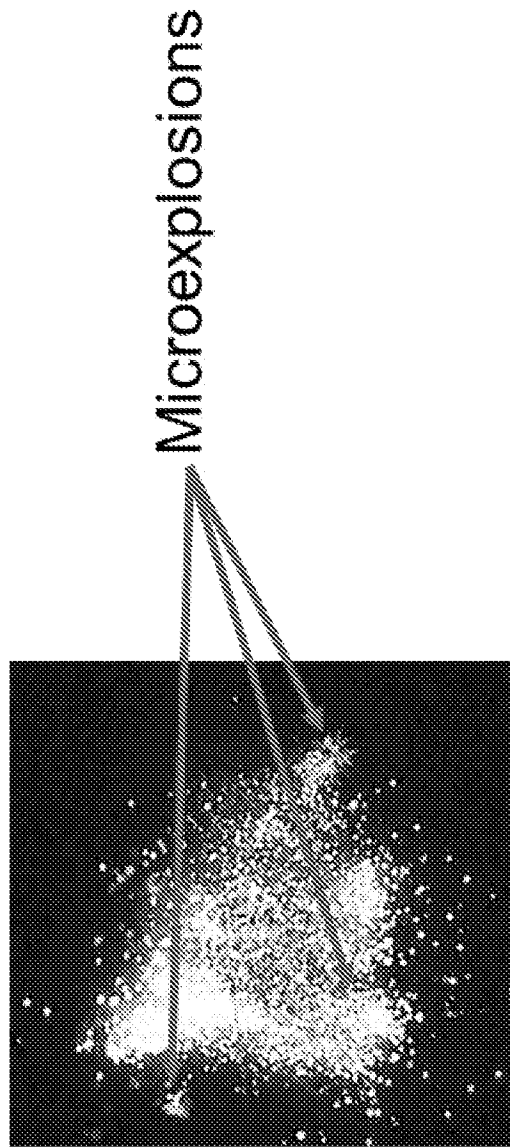


FIG. 6

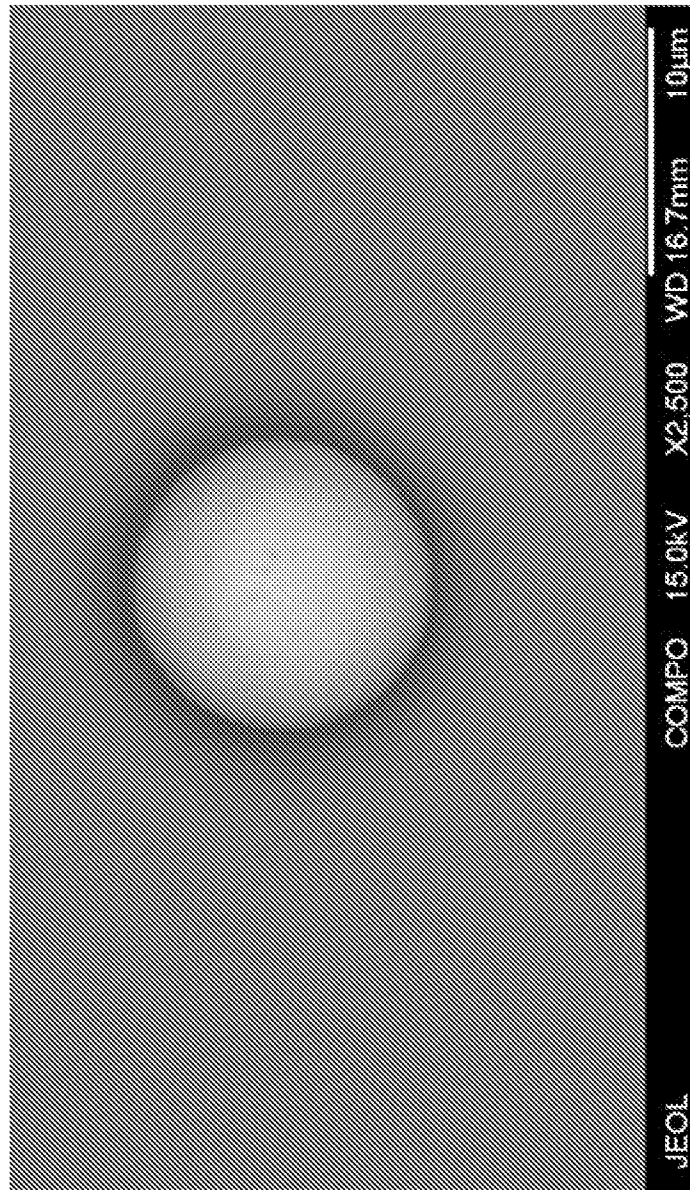
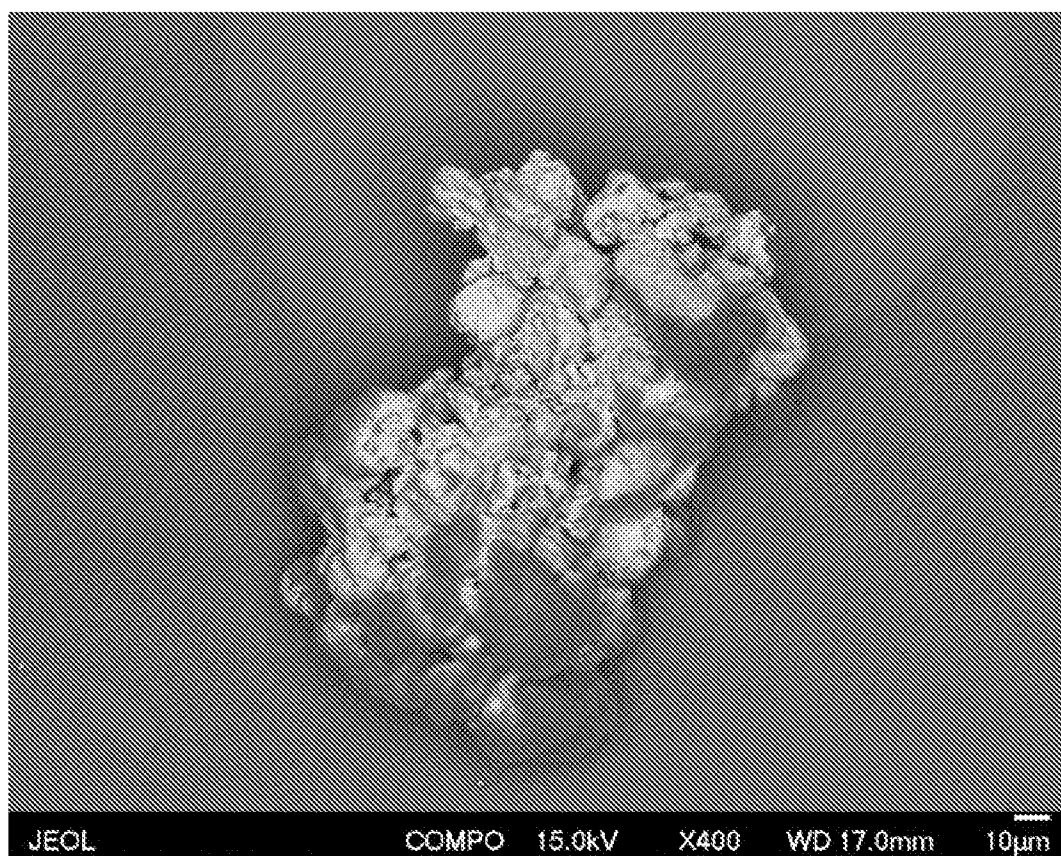


FIG. 7

**FIG. 8**

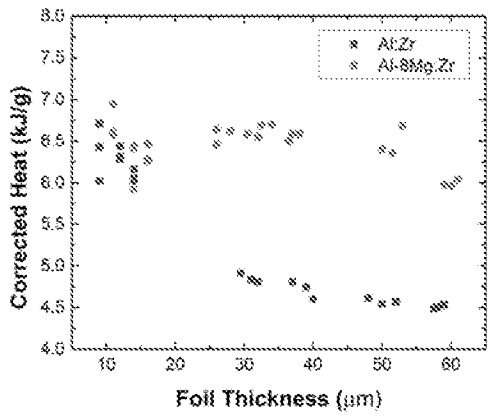


FIG. 9A

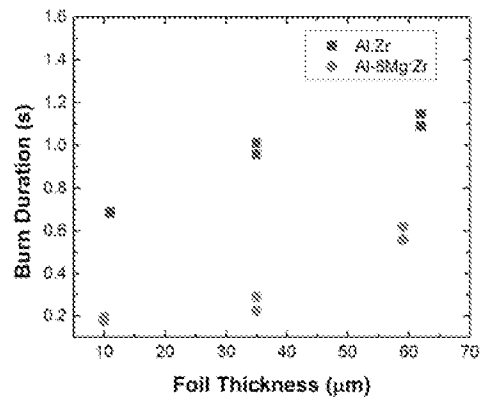
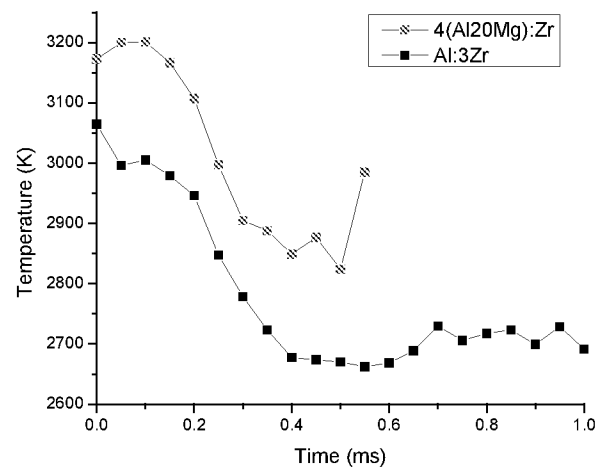


FIG. 9B

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**FIG. 10**